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# Spectroscopic and microscopic study of Prussian blue film for electrochromic device application



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## ABSTRACT

All solid electrochromic devices (ECDs) were prepared using Prussian blue (PB) as electrochromic layer, CeO<sub>2</sub>-TiO<sub>2</sub> as counter electrode and poly(vinylidene difluoride) (PVDF) as ionic conductive membrane. The electrodeposited PB films were characterized by ellipsometry and the thickness, roughness and refractive index of 217 nm, 1.9 nm and 1.5808, respectively, were obtained. The ECDs were assembled by combining the PVDF-based electrolyte membrane between the ITO-glass/CeO<sub>2</sub>-TiO<sub>2</sub> and PB/ITO-glass electrodes. From the electrochemical measurements, it was stated that applying potentials of +1.5 and –2.8 V promoted the color change of the ECD from blue to transparent. The UV–vis transmittance spectra revealed that applying 15 s/15 s and 60 s/60 s square wave of –2.8 and 2.0 V resulted in the difference of 15.9 and 39.6% between both states, respectively. Moreover, the charge density values increased from ~7 to ~10 mC cm<sup>–2</sup>, after applying –2.8 V for 15 and 60 s, respectively. The memory test of the ECD performed in open circuit, after applying –2.8 V for 15 s, revealed a decrease of transmittance from 37.5 to 21% in 24 h. The cyclic voltammetry performed at 100 mV s<sup>–1</sup>, evidenced the reduction at –0.1 V and oxidation at 0.4 V peaks, responsible for PB color change. Additionally, it was stated that after 500 chronoamperometric cycles, the charge density values decreased from –4.8 to –1.9 mC cm<sup>–2</sup>. Finally, the presented results suggest the possibility of using PB as electrochromic coating and PVDF as solid electrolyte in new ECDs development.

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## 1. Introduction

Prussian blue (PB) is a well-known material, and its discovery is dated to the 18th century by Diesbach [1], but even so, the electrochromic properties of this materials were observed by Neff [2] only in 1978. The first use of this blue colored material was for dyeing the uniforms of Prussian soldiers, thus was named Prussian blue. After that, it was used as carbon paper dye and also in paints and pigments [3]. The two forms of PB are called insoluble Fe<sup>III</sup><sub>4</sub>[Fe<sup>II</sup>(CN)<sub>6</sub>]<sub>3</sub> and the soluble MFe<sup>III</sup>[Fe<sup>II</sup>(CN)<sub>6</sub>], where M is an alkaline metal. However, recently it was reported that the PB's solubility is related mostly to its peptisation than to real solubility [4]. The PB's blue colored film can be obtained by electrodeposition, however the application of negative potential promotes the reduction of the PB to Prussian white (PW), Fe<sup>II</sup>[Fe<sup>II</sup>(CN)<sub>6</sub>]<sup>2–</sup>

and consequently turns the film transparent [5,6]. The positive potentials application causes the oxidation of PW back to PB [6].

Some studies of the thickness and roughness of PB films as results of SEM and AFM analysis have been reported [7]. The PB films were already studied by using ellipsometry [8] however, no data concerning PB morphology analysis using this technique have been found. The spectroscopic ellipsometry is an optical technique that uses polarized light for analyzing thin films, which thickness can vary from a few to thousands of Angstroms. This technique has been used for about a century, and today it is possible to determine the thickness, dielectric properties and roughness of the films [4]. The analysis of the film thickness also requires that a portion of the light pass through the film and come back to the film surface. If the material absorbs light, the measure is limited to thin and semi - opaque films [9].

PVDF is a non-reactive and pure thermoplastic fluorine polymer produced by polymerizing vinylidene difluoride. This polymer is used in applications requiring purity, strength, and resistance to acids, bases and heat. PVDF produces also low smoke quantity

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when burned. Moreover, this polymer has a low density of  $1.78 \text{ g cm}^{-3}$  and low cost compared with other fluorine polymers [10]. It is available as piping products, sheet, tubing, films, plates and insulation for premium wires [11,12]. It can be injected, molded or welded and is commonly used in chemical, semiconductor, medical and defense applications, as well as in lithium ion batteries [13]. PVDF is also available as a foam, increasingly used in aviation applications [10]. The preparation of PVDF is simple and more commonly performed by radical polymerization of 1,1-difluoroethylene [12]. The solvent for the synthesis is usually water with peroxy compounds acting as initiator. The structure of the monomer is  $-(\text{CF}_2-\text{CH}_2)-$ , and the chains are mainly in a configuration of head to tail [14].

More recently, PVDF started to be studied as gel-polymer electrolyte or porous membrane combined with different salts, like  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$  and  $\text{LiBF}_4$  [13,15–17]. Similarly, to other polymer electrolytes, including those based on natural polymers the main goal was to use them in electrochemical devices in substitution of liquid ones [18–20]. The preparation of solid PVDF membrane by mixing N-methyl-pyrrolidone (NMP) and ethylene carbonate (EC) and/or tetrahydrofuran (THF), and also  $\text{LiClO}_4$  was already described [15]. It was stated that ionic conductivity of those membranes depended on the added salt, but were all around  $1.8 \times 10^{-3} \text{ S cm}^{-1}$ . Another gel-type electrolytes based on PVDF and plasticizers such as ethylene carbonate (EC) and propylene carbonate (PC) with lithium salts showed favorable electrochemical properties, mainly high conductivity, mechanical and electrochemical stability [21].

Few papers concerning ECD with PVDF-based electrolytes were found. Among them, the report on the complementary electrochromic device with PEDOT:PSS/IL/PVDF-HFP electrospun membrane/PANI:DBSA that was assembled and tested spectroscopically at 695 nm under applied potential of  $-1.4$  and  $+1.4 \text{ V}$  [22] can be cited. This device showed the optical absorbance difference ( $\Delta A$ ) between colored and bleached states of 0.235 to 0.242 depending on the previous heat treatment of the PVDF-based membrane and no performance deterioration. Similar ECD with ITO-glass/PANI-DBSA/IL-loaded electrospun PVDF-co-HFP mat/PEDOT-PSS/ITO-glass configuration was reported recently [23]. This device revealed the maximum change in absorbance ( $\Delta A$ ) of 0.53 at 650 nm after potential switching between  $-1.5$  and  $+1.5 \text{ V}$ . The device with laminated layers of PET/ITO/ $\text{WO}_3 \cdot \text{H}_2\text{O}$ /Al grid/1-M  $\text{LiPF}_6$  EC/DMC-PVDF-HFP/Al grid/PANI/ITO/PET was also assembled and studied by cyclic voltammetry and UV-Vis-NIR spectroscopy after applying potentials of  $-1.5$  to  $+0.3 \text{ V}$  [24]. It was observed that the poor adhesion of the PVDF-HFP plastic film to the current collector as well as limited conductivity of the ITO-coated PET were responsible for low transparency and overall performance of this device. However, electrochromic efficiency was high regarding the light modulation in the NIR region due to the PANI secondary electrode and charge transfer was also improved due to the presence of Al grids.

Aiming to progress on the electrochromic devices research, the present paper describes the preparation, characterization and application of Prussian blue films in ECDs with glass/ITO/PB/PVDF-electrolyte/ $\text{CeO}_2$ - $\text{TiO}_2$ /ITO/glass configuration.

## 2. Experimental

PB films were obtained by applying cathodic current of  $-40 \mu\text{A cm}^{-2}$  for 300 s with an Autolab 302 N on glass/ITO (Delta Technologies; CG-50IN-1507; 8–12 ohms) working electrode in a solution containing 5 mL of HCl ( $0.05 \text{ mol L}^{-1}$ ), 10 mL of  $\text{K}_3\text{Fe}(\text{CN})_6$  ( $0.05 \text{ mol L}^{-1}$ ) and 10 mL of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  ( $0.05 \text{ mol L}^{-1}$ ) [5].  $1 \text{ cm}^2$  platinum plate was used as counter electrode and Ag/AgCl as reference electrode. After that, the glass/ITO/PB was withdrawn

from the solution and washed with Milli-Q<sup>®</sup> water. Stabilization of the films was performed by applying 10 cyclic voltammeteries in the potential range from  $-0.2$  to  $+0.6 \text{ V}$  in  $\text{KCl } 1 \text{ mol L}^{-1}$  solution.

The  $\text{CeO}_2$ - $\text{TiO}_2$  thin films were obtained by sol-gel process and deposited by dip-coating method with the withdrawal rate of  $20 \text{ cm min}^{-1}$  [25].

The polymer electrolyte was prepared by dissolving 1.5 g of PVDF in 5 mL of acetonitrile and 4 mL of poly(carbonate propylene) (PC) using magnetic stirrer. Then, 0.1 g of  $\text{LiClO}_4$  and 0.2 g of poly(ethylene glycol) (PEG) were added, mixed, versed on Petri dish and dried at  $40^\circ\text{C}$ .

The electrochromic devices (ECDs) with  $1 \text{ cm}^2$  area and having the glass/ITO/PB/PVDF-electrolyte/ $\text{CeO}_2$ - $\text{TiO}_2$ /ITO/glass configuration were obtained by assembling the two pieces of PB and  $\text{CeO}_2$ - $\text{TiO}_2$  coated glasses. One cm free space was left for the electrical contact. Then the  $\text{CeO}_2$ - $\text{TiO}_2$ /ITO-glass substrate was pressed onto the PVDF-membrane in such a way that the two coatings faced each other inside the assembled window. A 1 cm wide Cu-conducting tape (3 M) was glued to the free edge of each substrate for electrical connections. The mounted cells were finally sealed with a protective and insulating tape (3 M).

The ellipsometric measurements were performed with a Sentech SE 850 E equipment operated by SpectraRay 3 software. The measurements were conducted at  $0$ ,  $45$  and  $90^\circ$  of the glass/ITO/PB inclination and incident light at  $70^\circ$ . Measurements were performed with variation of the angle of incident light of  $40$  to  $70^\circ$ , with  $5^\circ$  step and the table switching between  $0$ ,  $45$  and  $90^\circ$ . The thickness distribution maps were obtained with ellipsometer mapping mode under angle of  $70^\circ$ . The thicknesses of all samples were checked in area equal to  $1 \text{ cm}^2$  in 25 points. The  $\mu$ -spots focused the light beam to diameter equal to  $200 \mu\text{m}$ . The values of layer thickness and roughness thickness were determined after measurement in every investigated point. The mentioned values were fitted with constructed sandwich model composed by air/roughness/Prussian blue/ITO/glass layers. The step-by-step measurements were carried out before use of mapping mode. First the glass substrate without ITO, next glass with ITO and finally Prussian blue layer was investigated. The Psi and Delta of the glass substrate and Prussian blue film were fitted with Cauchy model and the ITO layer results were fitted with Drude-Lorentz model. The value of refractive index at  $632.8 \text{ nm}$  was determined with Spectra Ray Software and was constant in infrared spectrum range too. The thickness in every point was determined for  $200 \mu\text{m}^2$  area.

The scanning electron microscopy (SEM) images of the PB films were obtained with LEO 440.

The atomic force microscopy (AFM) images were obtained with Digital Instruments Multi-Mode Nanoscope IIIa by using silicon AFM probes in the intermittent-contact mode; a force constant of  $48 \text{ N m}^{-1}$  and a resonance frequency of  $190 \text{ kHz}$ .

The cyclic voltammetry and chronoamperometric measurements of ECDs were performed with an Autolab 302N apparatus applying potential from  $-2.8$  to  $+1.5 \text{ V}$  and scan step of  $100 \text{ mV s}^{-1}$ .

The UV-vis spectroscopy measurements were recorded with an Agilent 8453 between 200 and 1100 nm and the memory test of the ECD was realized by measuring the transmittance at  $686 \text{ nm}$  in open circuit after application of  $-2.8 \text{ V}$  for 15 s.

*In situ* UV-spectroelectrocyclic voltammograms, recorded from 350 to 1000 nm in the potential range from  $-0.2$  to  $+0.6 \text{ V}$  in aqueous  $1 \text{ mol L}^{-1}$  KCl solution, were obtained in a quartz cell with two platinum electrodes with  $3.5 \text{ cm}^2$  each, as counter electrodes [26]. Those were positioned perpendicular to the optical path to free the passage of light and generating an homogeneous electric field on the surface of a conductive glass ITO, used as working electrode, located parallel to the optical path of the electrochemical cell with an area of  $0.5 \text{ cm}^2$ . A saturated calomel electrode was used as reference electrode, positioned close to the surface of conductive

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